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Title of Invention: Thermosetting resin composition

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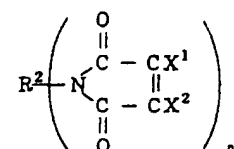
Specifications

1. Title of Invention:

Thermosetting resin composition

2. Claims:

1. A thermosetting resin composition, characterized in that it consists of (A) an amine adduct which is produced by (a) a diamine compound with the general formula $H_2N-R^1-NH_2$ (where R^1 is a bivalent organic group which has a carbon number of at least 2) and (b) an epoxy compound with at least 2 epoxy groups, and (B) a polyimide with the general formula



(where R^2 is an n-valent organic group, X^1 and X^2 are monovalent atoms or groups selected from hydrogen atoms, halogen atoms, or organic groups, which are the same or different, and n is an integer 2 or greater).

2. A thermosetting resin composition in accordance with Claim (1), in which the diamine compound in the amine adduct is 1.5–10 times the stoichiometric amount of the epoxy compound.

3. A thermosetting resin composition in accordance with Claim (1), in which the molar ratio of the amine adduct and the polyimide is in the range of 0.2:1–1.5:1.

3. Detailed Explanation of Invention:

Industrial Field of Application

This invention concerns a thermosetting resin composition with excellent workability and excellent heat resistance after it is set, which is soluble in low-cost solvents with low boiling points, such as ketones, in the B stage.

Prior Art

Polyimides of the dehydration condensation type and maleimides of the amine-setting type are well known as materials with heat resistance classifications of H or above, but amine-setting maleimides are becoming the more prominent type because they do not have problems such as condensation water. However, since they only dissolve in high-boiling-point solvents, their workability is poor and their properties cannot be used effectively.

Problems With the Prior Art

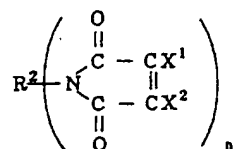
Three-dimensional polyimides, formed by thermally polymerizing poly-maleimides alone, are known as heat-resistant resins, but these three-dimensional polyimides have the drawback that they are extremely brittle, and they have not proved suitable for practical use. Furthermore, for amine-setting maleimides, [formed by] reacting polymaleimides and polyamines, aminobismaleimides, with bismaleimide skeletons, are primarily used. Aminobismaleimides form complex cross-linking bonds by the addition of amines and the radical polymerization of double bonds with each other, performed by heating prepolymers which have diamines added to the double bond of the bismaleimide; they are non-solvent, non-melting heat-resistant resins with excellent heat resistance. However, when they are used as solvent-type resins, they only dissolve in special, expensive bipolar solvents which have high boiling points, such as N-methyl-2-pyrrolidone and N,N'-dimethylformamide. Therefore, when the solvent is removed by drying, high temperatures are needed, and the residual solvent has effects on the properties of the product, so that this is a great obstacle to the workability and temperature resistance [of the product]. Otherwise, the aminobismaleimide resins have bad setting abilities; therefore, they have been modified by epoxy resins, but their solubilities in the solvents have not been improved.

Purpose of the Invention

This invention was made with the aforementioned drawbacks in amine-setting maleimides in mind. Its purpose is to provide a thermosetting resin composition which dissolves in low-boiling-point, inexpensive solvents, such as dioxane, methyl ethyl ketone, and methyl Cellosolve, have excellent workabilities, have excellent heat resistances, and are not adversely affected by residual solvents after molding is performed.

Outline of the Invention

The thermosetting resin composition of this invention is characterized by the fact that it consists of (A) an amine adduct which is produced by (a) a diamine compound with the general formula $H_2N-R^1-NH_2$ (where R^1 is a bivalent organic group which has a carbon number of at least 2) and (b) an epoxy compound with at least 2 epoxy groups, and (B) a polyimide with the general formula



(where R^2 is an n-valent organic group, X^1 and X^2 are monovalent atoms or groups selected from hydrogen atoms, halogen atoms, or organic groups, which are the same or different, and n is an integer 2 or greater).

Ordinarily, the amine adduct (A) can be obtained by reacting the diamine compound (a) and the epoxy compound (b) for a period from several minutes to several hours at a temperature in the range of room temperature to 250°C , either without a solvent or in a low-boiling-point solvent such as dioxane, methyl ethyl ketone, or methyl Cellosolve. The diamine compound is used effectively in a range of 1.5–10, preferably 2–8, times the stoichiometric amount of the epoxy compound. If the diamine compound is used at less than 1.5 equivalents with respect to the epoxy compound, it will gel easily during the reaction, and it will become difficult to control the reaction. If it is used at more than 10 equivalents, the solubility in the low-boiling-point, inexpensive solvents of the resin composition which is the final product of this invention will be reduced.

Moreover, the resin composition is obtained by heating and reacting the amine adduct (A) and the polymaleimide (B) in a ratio in the range of 0.2:1–1.5:1, at a temperature in the range of 50 – 200°C , for a period of time from several minutes to several hours, either without a solvent or in a low-boiling-point solvent such as dioxane, methyl ethyl ketone, or methyl Cellosolve. If the amine adduct is used at less than 0.2 mol, it will have inferior solubility in the low-boiling point solvent and the set article will become brittle. If it is greater than 1.5 mol, the heat resistance of the set article will be reduced and the effect of the invention will not be obtained.

Moreover, as a method of performing the heating and reaction in order to obtain the resin composition, one may react the diamine compound (a) and the epoxy com-

pound (b) beforehand to produce the amine adduct (A), and then add it to the polymaleimide (B) and perform the reaction, or one may synthesize the amine adduct (A) separately and then add it to (B) and perform the reaction.

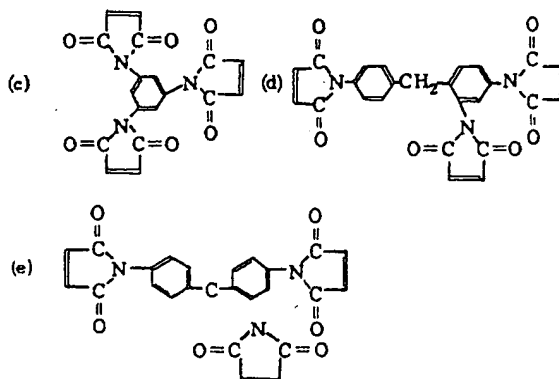
The diamine compound (a) constituting the amine adduct (A) of this invention may be one of the following compounds:

4,4'-Diaminodicyclohexylmethane, 1,4-diaminocyclohexane, 2,6-diaminopyridine, m-phenylenediamine, p-phenylenediamine, 4,4'-diaminodiphenylmethane, 2,2'-bis(4-aminophenyl)propane, benzidine, 4,4'-diaminophenyl oxide, 4,4'-diaminodiphenylsulfone, bis(4-aminophenyl)methylphosphine oxide, bis(4-aminophenyl)phenylphosphine oxide, bis(4-aminophenyl)methylamine, 1,5-diaminonaphthalene, m-xylylenediamine, 1,1-bis(p-aminophenyl)furan, p-xylylenediamine, hexamethylenediamine, 6,6'-diamine-2,2'-dipyridyl, 4,4'-diaminobenzophenone, 4,4'-diaminoazobenzene, bis(4-aminophenyl)phenylmethane, 1,1-bis(4-aminophenyl)cyclohexane, 1,1-bis(4-amino-3-methylphenyl)cyclohexane, 2,5-bis(m-aminophenyl)-1,3,4-oxadiazole, 2,5-bis(p-aminophenyl)-1,3,4-oxadiazole, 2,5-bis(m-aminophenyl)thiazolo(4,5-d)thiazole, 5,5'-di(m-aminophenyl)-(2,2')-bis(1,3,4-oxadiazole), 4,4'-diaminodiphenyl ether, 4,4'-bis(p-aminophenyl)-2,2'-dithiazole, m-bis(4-p-aminophenyl-2-thiazolyl)benzene, 4,4'-diaminobenzanilide, 4,4'-diaminophenyl benzoate, N,N'-bis(4-aminobenzyl)-p-phenylenediamine, 4,4'-methylenebis(2-chloroaniline), etc. These compounds may be used individually or in mixtures.

Examples of the epoxy compounds with at least 2 epoxy groups (b) of this invention are bifunctional epoxy compounds such as bisphenol A diglycidyl ether, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, 4,4'-(1,2-epoxyethyl)biphenyl, 4,4'-di(1,2-epoxyethyl)diphenylether, resorcin diglycidyl ether, bis(2,3-epoxycyclopentyl)ether, N,N'-m-phenylenebis(4,5'-epoxy-1,2-cyclohexanedicarboximide), etc., or trifunctional or higher epoxy compounds such as triglycidyl compounds of p-aminophenol, 1,3,5-tri(1,2-epoxyethyl)benzene, tetraglycidoxytetraphenyl ethane, phenolformaldehyde novolak resin polyglycidyl ether, etc. In addition, one may also use epoxy compounds with hydantoin skeletons and ones containing halogens. These compounds may be used individually or in mixtures.

Examples of the polymaleimides (B) of this invention are bismaleimides, such as N,N'-ethylenebismaleimide, N,N'-hexamethylenebismaleimide, N,N'-m-phenylenebismaleimide, N,N'-p-phenylenebismaleimide, N,N'-4,4'-diphenylmethanebismale-

imide, N,N'-4,4'-diphenylethylbismaleimide, N,N'-methylenebis(3-chloro-p-phenylene)bismaleimide, N,N'-4,4'-diphenylsulfonebismaleimide, N,N'-4,4'-dicyclohexylmethanebismaleimide, N,N'- α,α' -4,4'-dimethylenecyclohexanebismaleimide, N,N'-m-metaxylenebismaleimide, N,N'-4,4'-diphenylcyclohexanebismaleimide, etc.; triimides with the structural formulas (c)–(e) below



or poly(phenylmethylenepolymaleimide), etc. These compounds may be used individually or in mixtures. Furthermore, if desired, polymaleimides can be used together with monoimides, such as N-phenylmaleimide, N-3-chlorophenylmaleimide, or N-4-nitrophenylmaleimide.

The resin composition of this invention, which is obtained in this manner, is a thermosetting resin and is set by heating. This heating temperature should in general be in the range of 150–250°C. Furthermore, in order to accelerate the setting, one can add setting agents such as tertiary amines, imidazoles, peroxides, or organic acids to the aforementioned composition.

The quantity of the setting agent added should be in the range of about 0.01–0.5 wt % of the resin composition. Furthermore, one can also add suitable fillers, such as talc, alumina, silicon, zircon, quartz glass powder, glass fibers, etc.; coloring matters, such as carbon black or Bengal red; coupling agents, such as glycidoxypolytriethoxysilane; and mold release agents such as stearic acid.

The thermosetting resin composition of this invention has excellent heat resistance and solubility in low-boiling-point, low-cost solvents; it can be used in a wide range of applications such as laminating, adhesion, molding, etc.

Working Examples

Next, this invention will be explained in detail by giving working examples. The term "parts" below means "parts by weight," unless otherwise specified.

Working Example 1

One hundred ninety-eight parts (1 mol) 4,4'-diaminodiphenylmethane and 95 parts Epicote 828, a Shell Co. bisphenol A epoxy resin (190 epoxy equivalents) were mixed and reacted by heating and melting at 100°C for 1 hour to obtain an amine adduct. Furthermore, 716 parts (2 mol) 4,4'-diphenylmethanebismaleimide were added and the result was heated and melted at 100°C for 20 minutes to obtain a transparent red resin. This resin was soluble in dioxane, methyl ethyl ketone, and methyl Cellosolve with solids of 50 wt % or more.

Working Example 2

One hundred ninety-eight parts (1 mol) 4,4'-diaminodiphenylmethane and 72 parts DEN-438, a Dow Co. phenol novolak epoxy resin (180 epoxy equivalents) were mixed and reacted by heating and melting at 100°C for 1 hour to obtain an amine adduct. Furthermore, 716 parts (2 mol) 4,4'-diphenylmethanebismaleimide were added and the result was heated and melted at 100°C for 10 minutes to obtain a transparent red resin. This resin was soluble in dioxane, methyl ethyl ketone, and methyl Cellosolve with solids of 50 wt % or more.

Working Example 3

Two hundred sixty-seven parts (1 mol) methylenebis(o-chloroaniline) and 117 parts S-508, a Showa Denko Co. glycidyl ester epoxy resin (195 epoxy equivalents) were mixed and reacted by heating and melting at 150°C for 1 hour to obtain an amine adduct. Furthermore, 1067.5 parts (2.5 mol) N,N'-methylenebis(3-chloro-p-phenylene)-bismaleimide were added and the result was heated and melted at 130°C for 20 minutes to obtain a transparent red resin. This resin was soluble in dioxane, methyl ethyl ketone, and methyl Cellosolve with solids of 50 wt % or more.

Working Example 4

One hundred ninety-eight parts (1 mol) 4,4'-diaminodiphenylmethane and 76 parts Epicote 828 were mixed and reacted by heating and melting at 100°C for 1 hour to obtain an amine adduct. Furthermore, 928 parts (2 mol) poly(phenylmethylene)poly-maleimide were added and the result was heated and melted at 100°C for 20 minutes to obtain a transparent red resin. This resin was soluble in dioxane, methyl ethyl ketone, and methyl Cellosolve with solids of 50 wt % or more.

Next, the resins of Working Examples 1–4 were dissolved in a methyl ethyl ketone/dioxane (3:7) solvent to make varnishes. These varnishes were impregnated into an aminosilane-treated glass cloth (250 x 250 x 0.18 mm) and heating was performed at 130–150°C for 10 minutes to obtain a prepreg. Nine layers of this prepreg were laid on top of each other and press molding was performed at a temperature of 170–180°C and under a pressure of 40 kg/cm² to obtain a laminate 1.6 mm thick. The properties of this laminate are shown in Table 1.

Furthermore, for comparison, the properties of an imide laminate produced in the same manner as in the working examples by using a polyaminobismaleimide resin (Kermid 601, Rhône-Poulenc Co.) and N-methyl-2-pyrrolidone as a solvent, as well as an epoxy laminate (MEL-44A, Toshiba Chemical Co., MEMA rating G-10).